THE PHYSICS OF FERROELECTRIC MEMORIES

The ability of ferroelectric materials to switch robustly from one polarization state to another forms the basis of a new thin film technology for storing data.

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Imagine you are in the last stages of typing your thesis. The year is 1980, and it's a hot, hazy summer afternoon. A thunderstorm brews on the horizon. Tense and tired, you have forgotten to save the document on your hard disk. Suddenly, lightning strikes! Your computer shuts down. Your final chapter is lost.

Wistfully, you long for the day when everything you write is automatically stored in a nonvolatile memory system as soon as you write it and does not vanish if there's a power cut. What do I need to make this happen? you ask yourself. The answer is a fast, random-access, solid-state memory that is cheap, reliable and, most important of all, intrinsically nonvolatile—that is, it behaves like a magnetic disk storage system.

And while you're contemplating the electronic future, imagine also that you have an electronic smart card that you can use for everything from providing emergency crews with your health records to transacting all your expenses without having to sign a credit card slip or a check.

Now, fast-forward your mind to 1998, enter the new world of nonvolatile ferroelectric random-access memories—and read on!

Basic ferroelectric physics

Studied for a century, ferroelectric materials belong to a class of crystals whose low symmetry engenders a spontaneous polarization along one or more crystal axes. "Ferroelectric" is a misnomer, though an understandable one. Mathematically, ferroelectric and ferromagnetic materials can be described in the same way, and the hysteresis loops of polarization against electric field in the case of ferroelectrics are similar to those of magnetization against magnetic field for ferromagnetics. Confusingly for students, though, few ferroelectric materials contain any iron at all.

Ferroelectric crystals are characterized by having polarization vectors that can be oriented in two diametrically opposite directions (denoted by convention as + and –) by applying an external electric field. As shown in figure 1a, the + and – polarization states in a ferroelectric crystal are due to displacements of positive metallic and negative oxygen ions in opposite directions. This displacement automatically reduces the symmetry of the crystal—that is, from cubic to tetragonal. Thermodynamically stable, these states can be switched from one to the other by applying an external electric field known as the coercive field E_c.

Some ferroelectric materials—for example, $Pb(Zr_xTi_{1-x})O_3$ (PZT)—are transformed from a ferroelectric (low-temperature) phase to a nonferroelectric (high-temperature) phase at the "Curie temperature" (about 670 K for PZT). In addition, they typically exhibit polarization hysteresis. (See figure 2.) Other ferroelectric materials—$BaMgF_4$ (BMF), for example—do not exhibit such a phase transition, even up to their melting points.

Ferroelectric materials can have unit cell structures with different degrees of complexity—as can be seen in figures 1a and 1b, which show the unit cells of the cubic perovskite PZT and the layered perovskite $SrBi_2Ta_2O_9$ (SBT), respectively. In PZT, when a negative or positive voltage is applied on opposite faces of a crystal, the small Ti^{4+} or Zr^{4+} ions in the center of the cubic lattice are displaced up or down, while the O^{2-} ions move down or up. The displacement of the positive and negative ions results in the polarization that characterizes ferroelectric materials.

Usually, an as-grown ferroelectric crystal includes domains (regions with many unit cells containing ions displaced in the same direction) that have a mixture of polarizations. Some are up and down ("180° domains"), and others are perpendicular ("90° domains"). The process of orienting all the domains in one direction (up or down) is called poling. In ferroelectric materials, the domain walls have a net charge and are extremely narrow—often just one or two lattice spaces.

The ability of ferroelectric materials to switch their polarization direction between two stable polarized states provides the basis for the binary code-based nonvolatile ferroelectric random-access memories (NVFRAMs) that are the main subject of this article. Since domain walls move at about the speed of sound, they propagate across a one-micrometer film in about one nanosecond, thereby enabling nanosecond-speed memories.

How NVFRAMs work

Boolean algebra's "1" and "0"—the bases of digital computing—are stored in the capacitors of each NVFRAM memory cell as either a + or – polarization state of the ferroelectric layer. (See figure 1a.) In current devices, the memory cells are arranged in a square matrix. A 1-mega-

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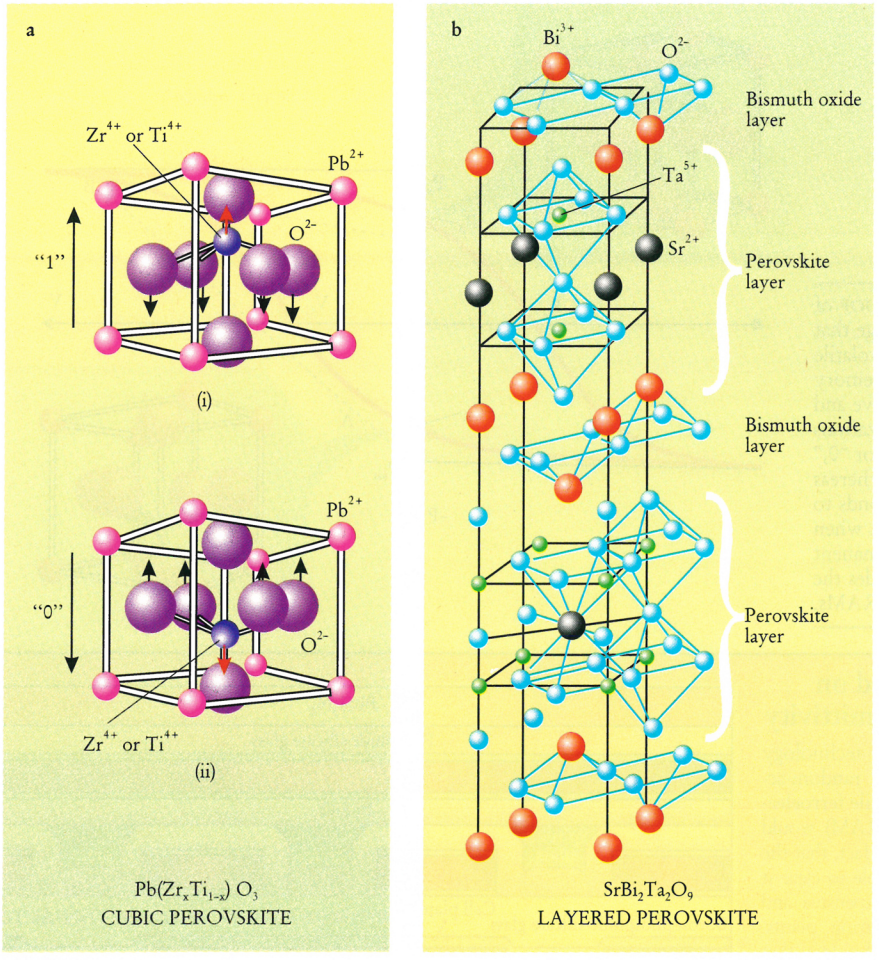


FIGURE 1. UNIT CELLS of two ferroelectric crystals. **a:** The cubic perovskite $Pb(Zr_xTi_{1-x})O_3$ shows polarization up (i) or down (ii) corresponding to, say, logic states "1" or "0," respectively. **b:** The layered perovskite $SrBi_2Ta_2O_9$ in a state of ionization. In this material, the layer of bismuth oxide helps to control the degradation of the polarization. PZT and SBT are the two main candidates for application in the first generation of NVFRAMs.

bit memory will therefore have 1000 rows and 1000 columns. To overcome the "crosstalk" problem that beset the early NVFRAM architecture, each memory cell capacitor is isolated from its neighbors by means of a passgate transistor. (See figure 3.) Each bit is written by applying half a short voltage pulse along a row (known as the bit line) and the other half along a column (the word line). Only at one particular addressed cell do the pulses add up to switch the polarization state.

Destructive and nondestructive reading schemes are being explored, although it appears that the first generation of NVFRAMs will be based on a destructive reading scheme. In this approach, the bit is read when a positive switching voltage is applied to the memory cell in the same way as the writing voltage described above. If the cell polarization is already + (representing, say, logic state 1), then only a linear nonswitching response is measured—in the form of a voltage across a 10–50–ohm resistor. If the cell is –, a switching response greater than the linear response is measured because it contains the additional displacement current term dP/dt, where P is the polarization. A sense amplifier then compares this response with that of a reference cell, which is always polarized +. Thus, the logic state 1 or 0 is read, and, in a destructive reading scheme, the memory cell reverts to the original 1 or 0 that was stored in the cell before the information was read.

The fact that ferroelectric layers can maintain an induced polarization, even in the absence of a voltage, provides the unique nonvolatility of NVFRAMs. Future personal computers based on NVFRAMs will not require backup disk memories. It is likely, therefore, that they will have no moving parts and be smaller and far more robust than today's PCs. Current fast-operating dynamic random-access memories (DRAMs) could be replaced by NVFRAMs. They could also be replaced with DRAMs based on another property of ferroelectric materials—namely, their high permittivity. (See box 1 on page 24.)

Early development

Before describing current issues in ferroelectric memories, we sketch the early development of these devices and the problems that have now been largely overcome—or at least better understood.

In the 1950s, the AT&T Co, Ford Motor Co, IBM Corp, RCA, Westinghouse Electric Corp and others made serious efforts to develop NVFRAMs. However, a number of factors prevented NVFRAMs from achieving commercial use—namely

▷ The NVFRAMs were based on expensive ferroelectric single crystals.

▷ Due to the thickness of the ferroelectric crystal, the coercive field of several kilovolts per centimeter required to switch the capacitor could be achieved only with voltages that significantly exceeded the 5-volt standard for silicon-based logic circuits.

▷ A simple row matrix address concept was devised in the 1950s, but it could not be successfully applied—mainly because of crosstalk. Memory cells addressed by applying half the switching voltage along the bit line and half along the word line would activate neighboring cells because the ferroelectric layer lacked a sharp voltage switching threshold E_c. Called half-select disturb-pulse, this kind of crosstalk affects the memory cells next to the one selected for full

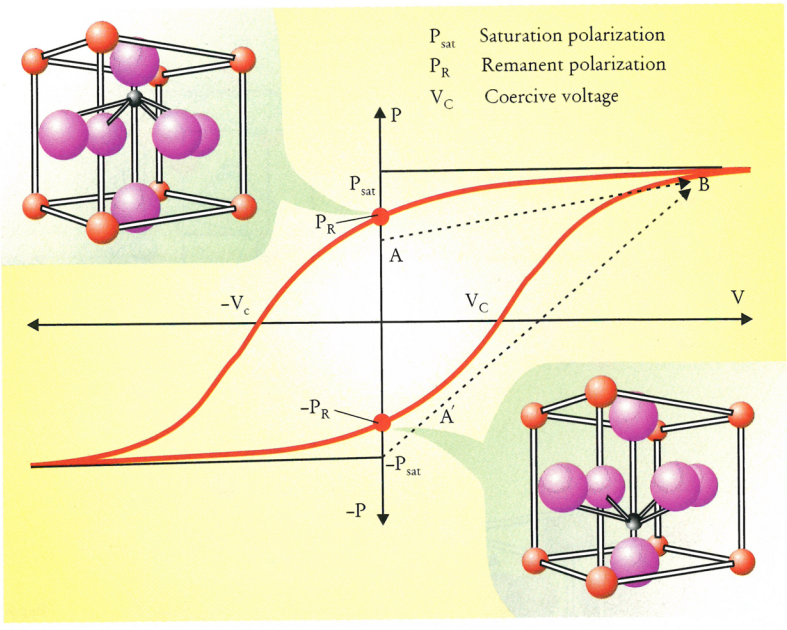


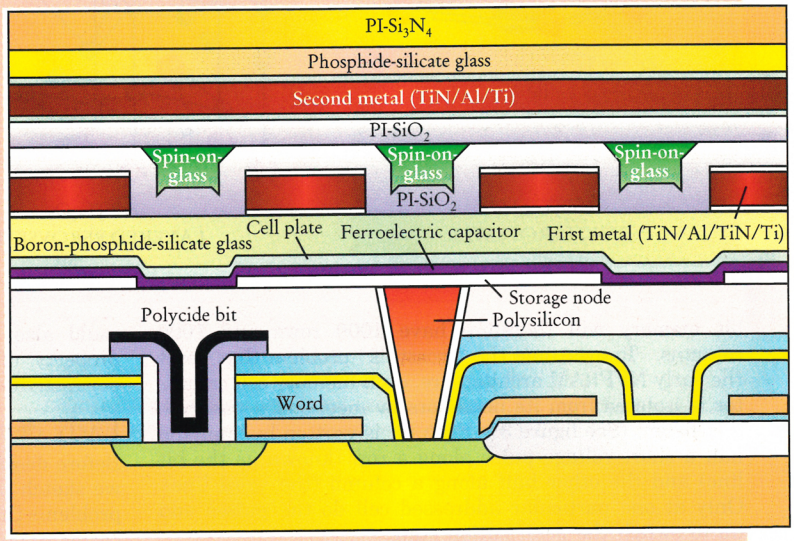
FIGURE 2. TYPICAL HYSTERESIS LOOP of polarization against voltage that represents the operation of an nonvolatile ferroelectric random-access memory (NVFRAM) capacitor. The positive and negative saturation polarizations correspond to the logic states "1" or "0," respectively, of the memory cell, whereas the remanent polarization corresponds to the state the memory cell resides in when the voltage is turned off. The remanent state is the one that provides the nonvolatility of NVFRAMs.

Box 1: DRAMs Based on Materials with High Permittivity

A change in computer memory technology from conventional dynamic random-access memory (DRAM) to nonvolatile ferroelectric random-access memory (NVFRAM) would be a great leap forward—so great, in fact, that the computer industry would not be able to clear it quickly, for it would entail the expensive and large-scale retooling of manufacturing plants. There is, however, a ferroelectric technology that is much closer than NVFRAM to conventional DRAM—namely, high-permittivity DRAM.

A ferroelectric material generally has a high permittivity ε, which can be exploited to store information as charge. Unlike NVFRAMs, in which the ferroelectric material is switched between polarization states, the polarization of a high-ε layer depends linearly on the applied voltage, as required for charging the DRAM capacitors. The high-ε materials used for DRAMs should not, therefore, exhibit polarization–voltage hysteresis loops. And to be effective, the high-ε material should also have a high breakdown field and a great resistance to charge injection.

High-ε DRAMs work in the same way as conventional DRAMs, in which a capacitor made from a layer of low-ε material—silicon dioxide (SiO_2), for example—is charged to record a logic state "1" or "0." However, this charge must be refreshed many times per second (that's where the "dynamic" part of the name comes from), due to the large leakage of current out of the capacitor. The transistor and resistors in a DRAM occupy a small percentage of the space in the chip, most of which is occupied by the low-ε capacitor. In general the capacitance of DRAM capacitors C is given by $\varepsilon AQ/t$, where A is the area covered by the layer, Q is the total charge and t is the layer thickness. Conventionally, the route taken to increase C (and, therefore, the amount of information stored) is to increase A, but doing so results in convoluted geometries that are hard to fabricate for gigabit DRAMs. Despite its small permittivity, SiO_2 does, however, have the advantage of presenting a superb barrier against charge injection.



An alternative way to increase C is to use materials with higher permittivities. Barium strontium titanate (BST), for example, has a relative permittivity $\varepsilon/\varepsilon_0$ of 300–400, compared with 7 for SiO_2. Accordingly, a BST capacitor could be fifty times smaller than one of the same capacitance made from SiO_2. With the aim of exploiting this advantage, extensive research is being performed to integrate ferroelectric materials into DRAM capacitors.[1]

In addition to having potential application to DRAMs, high-ε BST-based capacitors can be integrated with gallium-arsenide microwave monolithic integrated circuits (MMICs); in fact, such devices are now being produced commercially in Japan for use in cellular phones. Although BST capacitors have not been included in commercial DRAMs yet, it is unlikely that high-megabit to gigabit memories will be made without them. A diagram of a prototype Matsushita 64-megabit DRAM memory based on BST capacitors is shown in the accompanying figure (courtesy of Matsushita Electric Co).

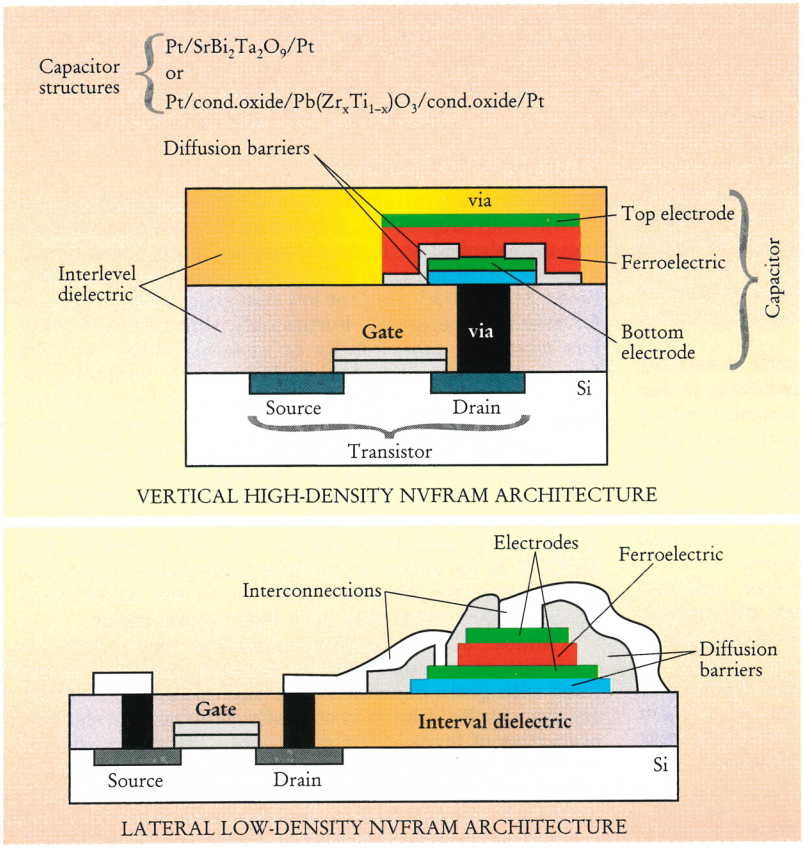


FIGURE 3. SCHEMATIC DIAGRAM of two kinds of nonvolatile ferroelectric random-access memory (NVFRAM) architecture. The high-density architecture (top) is designed for use as computer memory. The low-density architecture (bottom) is for smart cards and other applications of embedded memories, such as microprocessor controllers. Both architectures are examples of 1T–1C design—that is, each memory cell contains one transistor and one capacitor. This configuration helps to prevent crosstalk between adjacent cells.

voltage application.

The switching time depends linearly on the time over which the voltage pulse is applied and exponentially on the maximum amplitude of the electric field generated in the ferroelectric layer. For any given applied field (which could be well below E_c), there is a finite probability that the ferroelectric layer will switch its polarization state if the field is applied for long enough.

The present solution to the half-select disturb-pulse problem involves the use of a passgate architecture in which each ferroelectric capacitor cell is isolated from its neighbors by a transistor. (See figure 3.) Since it has one transistor and one capacitor per bit, this NVFRAM architecture is called 1T–1C. It can be fabricated in megabit and gigabit capacities through modern ultralarge-scale integration microcircuit technology. (An alternative architecture involves two capacitors per bit, one of which is a reference capacitor; this cell is more reliable for reading, but takes up more space.)

▷ Minimizing the various kinds of capacitor degradation proved elusive in the 1950s, as did extending the polarization retention time to the several years necessary for a nonvolatile device. The degradation processes consist of ferroelectric fatigue (the decrease in the amount of charge switched as a function of switching cycles), imprint (the tendency of a ferroelectric layer to revert to a preferential polarization direction once it has been switched to the opposite one) and leakage currents.

The thin film answer

The problems described above have been solved by using thin film technology. In particular, materials integration strategies developed during the past seven years have gained control of the capacitor degradation processes. In the case of capacitors based on PZT film, oxygen vacancies[2] and charge injection at the ferroelectric–electrode interface—the phenomena that cause degradation—are controlled by using conductive oxide electrodes, or hybrid oxide–platinum electrodes[3,4] where the oxide electrode layer is in contact with the PZT film. In the case of the layered perovskite SBT, it is the material's microstructure—an oxygen-rich bismuth layer, in particular—that controls degradation.[5] (See figure 1b.)

We do not understand polarization retention (or the loss of polarization) in ferroelectric capacitors as deeply as the degradation processes. Recently, nanoscale imaging of ferroelectric domains,[6] using a piezoresponse atomic force microscope, have suggested that retention loss may be controlled by a type of random walk depolarization process.

Obviously, further work is necessary to unravel the details of the degradation processes, since they have important implications for ferroelectric memory technology. Even so, optimized prototype NVFRAMs with passgate architecture can currently sustain 10^{14} successive read–write operations with negligible imprint, long polarization retention and without noticeable fatigue.

Unsolved physics

Besides degradation and polarization retention, there are four basic physics-related issues that challenge our current understanding of the physics of ferroelectric thin films and memory-related phenomena.

First, What is the ultimate polarization switching speed, and what parameter limits speed? According to theoretical calculations, the switching time in very small capacitors is limited by the time taken by polarization domains to nucleate, rather than by the speed of the domain walls. Using experimentally measured domain nucleation rates for PZT capacitors,[7] one of us (James Scott) has calculated the ultimate switching speed for PZT capacitors to be 600 ± 200 picoseconds.[8] Actual switching speeds that have been measured by different groups are about 900 ps.[9] It is important to compare the switching speed of PZT capacitors with the fundamental speed of a ferroelectric memory. In a random-access memory (RAM), the ultimate performance speed is limited not by the access time, but by the interconnect time (about 200 ps) taken by the current from one transistor to charge the gate of the next. Since the 600 ps charging time for ferroelectric

capacitors is already near the interconnect time, switching does not intrinsically limit device speed.

Second, What is the thinnest ferroelectric layer that can still yield stable polarization? Theoretical work performed at IBM[10] indicated that the answer depends partly on the nature of the electrodes. With semiconducting electrodes, depolarization fields in a typical ferroelectric capacitor would destroy the polarization switching properties of layers thinner than 400 nm. With metallic electrodes, however, layers as thin as 4 nm can maintain switching. Subsequent theories proposed a limit of 2.5 nm,[11] but experiments have pushed it down even further: Functioning ferroelectric layers thinner than 0.9 nm have been produced in the laboratory.

Third, How do switching parameters, such as coercive field, depend on frequency? Polarization switching is due to domain motion in a lattice of finite viscosity, which always depends on frequency and rises with increasing frequency. Using hysteresis parameters measured at 50 Hz to predict device behavior at 100 MHz is therefore inappropriate. Theory predicts[12] that $E_c \propto f^{1/n}$, where f is the frequency and $n = 6$. The first experiments yield $n = 7 \pm 1$, in reasonable agreement with theory.

Fourth, What are the effects of finite size, and how small can a ferroelectric capacitor be and still exhibit ferroelectric behavior? NEC has reported switched polarization values for PZT capacitors as small as $0.7 \times 0.7 \times 0.2$ μm^3. Mitsubishi Electric Corp and Symetrix have fabricated patterned arrays of 1.0 μm capacitors.[13] And recently, polarization switching was measured in SBT capacitors fabricated with $0.1 \times 0.1 \times 0.05$ μm^3 electrodes of bismuth oxide. For a practical 1-gigabit NVFRAM, the individual ferroelectric capacitors must be less than 1 μm across and about 50 nm thick. The effects of such constrained geometries on ferroelectric capacitors are still largely unknown.

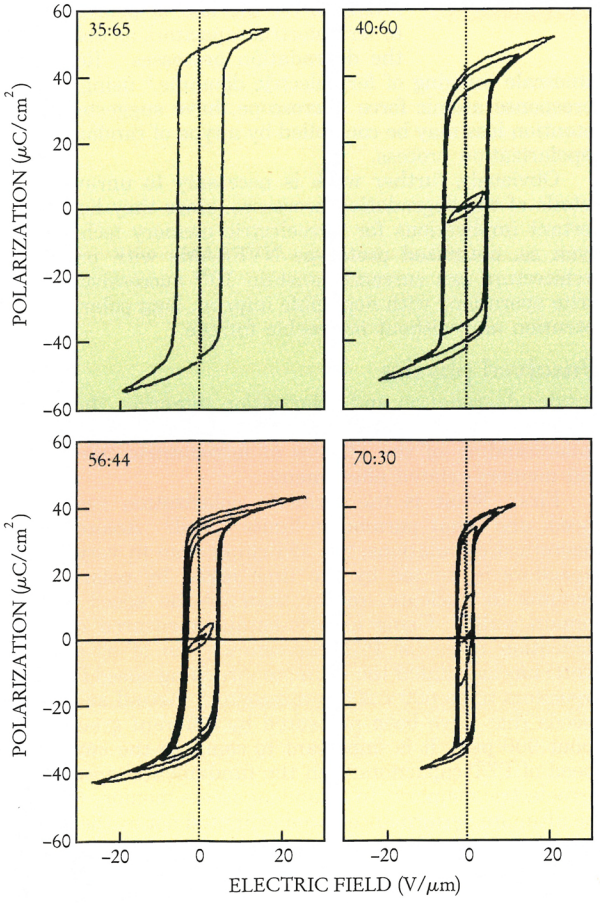


FIGURE 4. POLARIZATION HYSTERESIS LOOPS for four single-crystal PZT films with different ratios of zirconium to titanium grown on $SrRuO_3$ electrode layers. Single-crystal ferroelectric films can exhibit properties similar to those of bulk films, including the square hysteresis loops and sharply defined coercive fields shown here. In some respects, single-crystal films would make a better choice for nonvolatile ferroelectric random-access memories (NVFRAMs), since they can have higher and longer-lasting polarizations than bulk polycrystalline films. However, even the thinnest single-crystal films have much higher coercive fields than bulk films,[14] a property that limits their usefulness for low-voltage NVFRAMs. (From C. M. Foster *et al.* J. Appl. Phys. **81**, 2349, 1997.)

Thin film technology

The current operating voltage for computer memories (5 V) will soon drop to 3.3, 2.5 and 1.1 V. At these voltages, the ferroelectric or high-permittivity layers (see box 1) must be no thicker than 200 nm to sustain the low coercive fields (about 40 kV cm^{-1}) or low charging voltages required for efficient operation. Fortunately, thin film technology has advanced substantially on several fronts, including the development of several techniques for producing device-quality layers—namely, sputter and laser ablation deposition, metal organic decomposition, metal organic chemical vapor deposition (MOCVD), chemical vapor deposition and liquid solution synthesis.[3,4]

Of all these methods, MOCVD is the most suitable for producing ferroelectric layers and high-permittivity layers in an industrial process. A major advantage of MOCVD is its ability to produce high-quality crystalline ferroelectric thin films (see figure 4), as well as conformal layers on structures that have high aspect ratios.

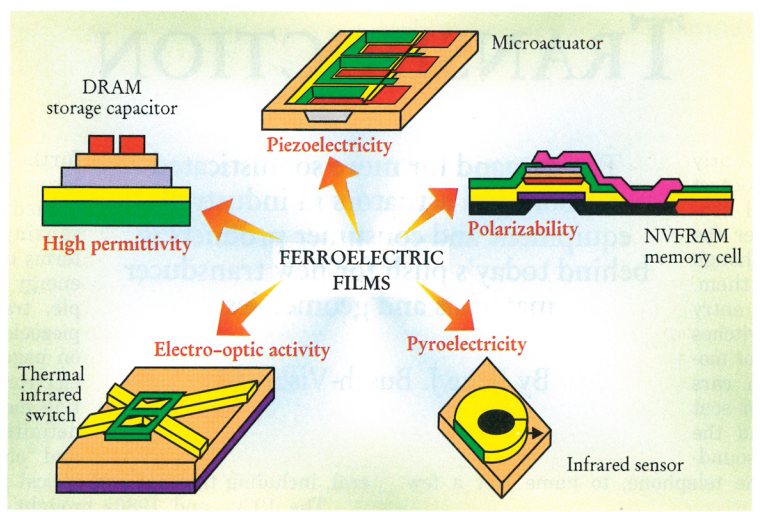
Almost all the methods described above have the capability of producing highly oriented, pseudo-epitaxial films with grain boundaries and intergrain depletion layers that can be tailored to critically influence the electrical properties of ferroelectric capacitors. Physicists with expertise in oxide perovskites, film synthesis methods and epitaxy can continue to play a key role in advancing the basic and applied science of ferroelectric thin films and memories. (And other applications—see box 2 on page 27.)

Industrial fabrication

The integration steps and tools required for the fabrication of NVFRAMs and high-permittivity DRAMs are similar. They should be scalable to large-area wafers, should introduce as few defects as possible and should have high throughput and high yield. Most likely, the ferroelectric or high-permittivity layers will be deposited onto a silicon wafer with a completed structure of complementary metal–oxide semiconductor. Such a process route is called back-end processing, and has the advantage that the wafers do not go back into a silicon processing fabrication line after the ferroelectric or high-permittivity layers are deposited. (This process route also avoids cross-contamination.)

Box 2: Other Applications of Ferroelectric Materials

Besides having application for computer memories, ferroelectric materials, particularly thin films, can be employed in the manufacture of a variety of other devices that exploit their special properties. Some of these properties are described below, together with examples of their application in devices whose commercial development shows great potential. (See also the accompanying figure.)



Ferroelectric materials also manifest piezoelectricity, a property that can be made use of in the manufacture of micromachines, such as accelerometers, displacement transducers and actuators of various kinds—including those required for inkjet printers, VCR head positioning and micromachining. There are two kinds of piezoelectricity. In direct piezoelectricity, a ferroelectric layer physically expands or contracts when a voltage is applied across it (as in actuators, for example). In indirect piezoelectricity, a voltage arises between the parallel opposite faces of a ferroelectric layer when the layer is compressed (as in pressure sensors, for example). (For more on piezoelectric actuators, see the article by Ilene Busch-Vishniac, beginning on page 28.)

Pyroelectricity, another property of ferroelectric materials, can be used as the basis for highly sensitive infrared room temperature detectors. The pyroelectric effect takes the form of a voltage between opposite faces of a ferroelectric layer when heat causes positive and negative ions to drift to opposite faces of the crystal. In this case, the dielectric material is defined as an electret.

Ferroelectric materials also exhibit electro-optic activity—that is, their refractive indices change when a voltage is applied across them. This effect can be used in color filter devices, computer displays, image storage systems and optical switches for integrated optical systems.

That these applications of ferroelectric thin films are only a few of those on a growing list indicates the increasing importance of these materials.

At present, several manufacturers use many schemes, none of which is necessarily optimized. Intensive research is currently under way to overcome the remaining problems that hinder the development of high-density ferroelectric memories.

Looking ahead

Our understanding of the physics of ferroelectric thin films has advanced substantially in the last decade. Thanks to this progress, ferroelectric capacitors can now be made and integrated with silicon-based integrated circuit technology to fabricate ferroelectric memories.

Now that the primary source of funding for this field has shifted from government to industry, several memory manufacturers are currently in the race to bring NVFRAMs and high-permittivity DRAMs to market. And the materials integration strategies already developed are being implemented to embed 64-kilobit ferroelectric memories in microchip controllers.

Further basic research is needed to better understand degradation phenomena in the submicrometer devices necessary for high-density memories. Also important is the development of appropriate diffusion barrier layers for the integration of ferroelectric capacitors with silicon.

Nevertheless, in the memory market of the 21st century, which is expected to be much bigger than the current worldwide level of $60 billion per year, ferroelectric materials will potentially play a significant, maybe even a starring, role.

References

1. A. I. Kingon, S. K. Striffer, C. Basceri, S. R. Summerfelt, MRS Bulletin **21**, 46 (1996).
2. D. Dimos, H. N. Al-Shareef, W. L. Warren, B. A. Tuttle, J. Appl. Phys. **80**, 1682 (1997).
3. MRS Bulletin **21** (6), (7) (1996), O. Auciello, R. Ramesh, eds.
4. O. Auciello, K. D. Gifford, A. R. Krauss, in *Ferroelectric Thin Films: Synthesis and Basic Properties*, C. A. Paz de Araujo, J. F. Scott, and G. W. Taylor, eds., Gordon and Breach, New York, N.Y. (1996) p. 393.
5. J. F. Scott, F. M., C. A. Paz de Araujo, M. C. Scott, M. Huffman, MRS Bulletin **21**, 33 (1996).
6. A. Gruverman, H. Tokumoto, A. S. Prakash, S. Aggarwal, B. Yang, M. Wuttig, R. Ramesh, O. Auciello, T. Venkatesan, Appl. Phys. Lett. **71** 3492 (1997).
7. H. M. Duiker, P. D. Beale, J. F. Scott, C. A. Paz de Araujo, B. M. Melnick, J. D. Cuchiaro, L. D. McMillan, J. Appl. Phys. **68**, 5783 (1990).
8. J. F. Scott, Ferroelectric Reviews **1**, 1 (1998).
9. P. K. Larsen, G. L. M.Klampschoer, M. J. E. Ulenaers, G. A. C. M. Spierings, R. Cuppens, Appl. Phys. Lett. **59**, 611 (1991).
10. I. P. Batra, B. D. Silverman, Solid State Commun. **11**, 291 (1972).
11. T. Yamamoto, Integrated Ferroelectrics **12**, 161 (1997).
12. Y. Ishibashi, H. Orikara, Ferroelectrics **9**, 57 (1995).
13. H. Uchida, N. Soyama, K. Kageyama, K. Ogi, M. C. Scott, J. D. Cuchiaro, G. F. Derbenwick, L. D. McMillan, C. A. Paz de Araujo, Integrated Ferroelectics **16**, 41 (1997).
14. W. J. Merz, Phys. Rev. **95**, 690 (1954). ■